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Project Summary

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Analytical Methods for Hazardous Organics in Liquid Wastes from Coal Gasification and Liquefaction Processes

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This report describes the progress made in developing a systematic analytical protocol for identifying and quantifying predominant hazardous organic chemicals present in the wastewaters of coal gasification and liquefaction plants. The first phase consisted of development of a qualitative scheme including chromatographic separation, total organic carbon determination, infrared spectrometry (IR), gas chromatography and mass spectrometry (GC-MS). An additional task of testing coal liquids, the raw end products of coal liquefaction, for mutagenicity was carried out. Minimal mutagenicity was found in three out of four water extracts taken from coal liquids.

The second phase consisted of the quantitation of the compounds detected in the wastewaters. Twenty hazardous organic chemicals named in the USEPA priority pollutant list were detected in varying quantities in the wastewaters. Polynuclear aromatic hydrocarbons (PAH) were found to be present in concentrations yielding gram quantities in daily operation of an average pilot plant. Nitrogenous compounds were present at the same level, and one in particular, N-nitrosodimethylamine, was present at kilogram levels daily. Phenol was present in concentrations high enough to be potentially recoverable economically. Phenolic compounds were the most predominant organic species found.

Method development incorporated the use of macroreticular resins for the initial separation of the organics in the wastewaters, sensitive GC-MS and IR identification, and quantitative computer matching mass spectra. A protocol of methods will be assembled into handbook form for the third phase of this study. Further analysis of coal wastewaters for organometallics, metals and heteroatomic organics will also be carried out in this phase.

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This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Gasification and liquefaction of coal will generate hundreds of organic species which will contaminate the

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water associated with the conversion processes, and pose a possible threat to the environment.

A majority of coal plant waste streams released into the environment are wastewaters from coal conversion process steps (Oak Ridge National Laboratory, 1977).[1] This includes wastewater originating as moisture in coal, water of constitution or decomposition, water added for stoichiometric process requirements, and water introduced by product recovery or gas scrubbing. These types of wastewater contain soluble and suspended organics and are produced in both the coal gasification and liquefaction processes. These wastewaters are formed under the following conditions:

1. When gases are scrubbed to remove soluble contaminants, quenched to control operating temperature, compressed, or dehydrated;
2. When steam used in the unit process cools and condenses or is reformed during methanation or hydrotreating;
3. When the product oil is formed by hydrogenation or pyrolysis and is allowed to settle for product recovery; or
4. When slags and ash are water-quenched for slurry removal.

The contaminant content of wastewater varies according to feed coal ranks, conversion process types and severity, and upstream subsidiary treatments. This wastewater is usually also heavily laden with inorganic cations and anions which may consequently form double salts and complexes; so the specific relationship of the inorganics to the dissolved organic species further complicates the problems of treatment and abatement.

The chemical species are varied and numerous because they represent practically all the organic compounds found in coal (Rubin and McMichael, 1975).[2] The structure of coal, as recently proposed (Victor, 1977)[3] can be visualized as consisting of islands of aromatic and heterocyclic clusters connected by weak linkages, such as hydrogen bonding, quaternization, or donor-acceptor complexation (Yen, 1976).[4] The coal conversion processes involve a variety of reactions with pressure, heat, catalysts, and/or water. These reactions produce many classes of organic species. Some of the typical compounds identified (Peterson, 1975)[5] are PAH, phenolics, nitrogenous compounds, other oxygen-functional compounds, and organometallics, which fall under the classification of potentially hazardous materials (USEPA, 1975).[6]

The overall objective of this project was to develop analytical methods enabling identification and analysis of hazardous organic compounds in wastewater effluents from coal conversion processes. A systematic scheme of isolating hazardous compounds as well as study of their nature and properties would help in designing a treatment method later. Development of a complete protocol for major hazardous compounds will lead to monitoring and controlling them so that potential hazards to human health and the general environment may be minimized.

The research work consisted of three phases:

1. Development of a systematic scheme of separation and identification for the following four types of hazardous compounds:
   a. PAH
   b. phenolics
   c. nitrogenous compounds
   d. other oxygen functional compounds
2. Quantification of the identified species in various coal waste effluents.
3. Development of a complete protocol in handbook form for all hazardous compounds mentioned in Phase One and also including:
   e. organometallics
   f. metals
   g. other species identified in this study and known to be hazardous.

This report pertains to Phase One and Phase Two.

Procedure

The first classification step was the separation of the organic compounds into hydrophobic and hydrophilic compounds by passage through an Amberlite XAD-8 macroreticular resin. Further classification was based upon acid/base characteristics. Hydrophobic acids and bases were desorbed by aqueous alkali (0.5 N NH_2OH) and acid (0.1 N HCl), respectively. Hydrophobic neutrals were eluted with methanol. Hydrophilic acids and bases were adsorbed on cation and anion exchange resin and eluted in 0.5 N NH_4OH. Hydrophilic acids were concentrated on OH⁻-form AG MP-1 anion exchange resin and eluted with 0.5 N HCl. Hydrophilic neutrals passed through all columns and were collected (Figure 1).

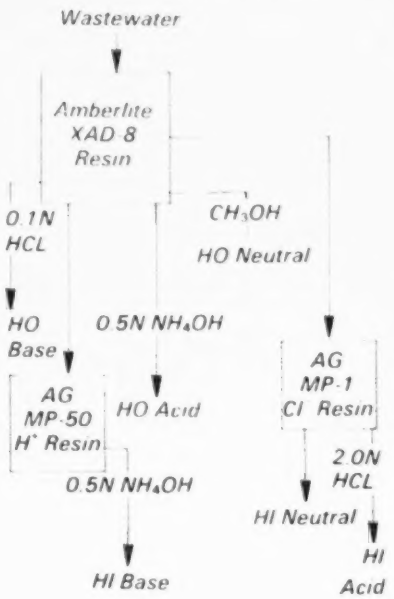

Figure 1. Flow diagram of column adsorption to separate organics in coal process water.

The XAD-8 resin was supplied as an industrial grade product (20-40 Tyler mesh) which was purified by first rinsing with 0.1 N NaOH, 0.1 N HCl, and then by Soxhlet extracting successively for 24 hours using acetonitrile, ethyl ether, and methanol. The resin was then packed in a column rinsed with distilled water, and tested for organic compounds prior to usage.

The AG MP-50 and AG MP-1 resins were washed successively with 1 N HCl, 1 N NaOH, and then Soxhlet extracted successively for 24 hours in methanol, methylene chloride, and n-pentane prior to use as column packing. Test samples of model compounds were made and the extent of the separation was noted prior to usage.

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To identify the many compounds contained in each fraction produced by the resin chromatographic separation, a GC/MS equipped with a computer library of mass spectra of 31,331 compounds was used. The peaks eluting from the GC can be individually and immediately analyzed for their mass spectra which can then be compared to those in the computer library. The three best matching spectra are then printed for visual inspection.

A quantitative assessment of the match between the sample peak spectrum and a given library spectrum is provided in the "fit," "reverse fit," and "purity" indices. These are based on scales of 1 to 1000. "Fit" describes how well the library spectrum fits into the sample spectrum. "Reverse fit" describes hov well the sample spectrum fits into the library spectrum. "Purity" is the Boolean algebra dot product of the two. While fits should be in the 800's and 900's for confidence in identification, a lower purity index need not discount the match. Purities can very rarely be above 900, so values between 500 and 900 merit confidence if their fits are good. In some cases, the discretion of the mass spectroscopist is called into play to choose among closely ranking matches.

Not all the data and spectra match candidates will be presented here. Survey analysis summaries of the best matches for each peak with their fit, reverse fit, and purity indices, are presented in Tables 1 through 6 of one

Table 1. *Percentage of Total Organic Carbon Distribution in Separated Fractions*

Separated Fraction	% of Origin In-Put TOC* No. 1	No. 2
HI acid	2.7	3.4
HI base	2.4	6.8
HI neutral	10.7	15.2
HO acid	9.4	14.5
HO base	7.1	12.6
HO neutral	48**	40**

*The original input TOC for No. 1 and No. 2 are 2083 ppm, 1755 ppm, respectively.

**Values approximated from GC peaks of solvent.

Table 2. *GC-MS Computer Match Summary Hydrophobic Neutral Fraction of Water Sample No. 1*

Compound	Peak No.	Purity	Fit	Reverse Fit
Methylbenzene	77	965	981	977
Ethyl acetate	131	903	951	916
Methoxybenzene	193	897	977	917
Phenol	244	769	902	775
2-Methylphenol	264	949	982	960
3-Methylphenol	286	938	982	947
3,5-Dimethylphenol	303	914	980	914
2,5-Dimethylphenol	315	879	978	879
3,4-Dimethylphenol	324	933	997	933
4-(1-Methylethyl)phenol	331	751	810	818
2-Ethyl-5-methylphenol	335	788	881	881
2-Ethyl-4-methylphenol	343	828	922	861
4-Ethyl-2-methylphenol	352	869	961	885
3,4-Dimethylbenzaldehyde	382	808	989	808
Pentamethylbenzene	394	762	902	788
3-Phenylfuran	451	846	974	862
(1,1'-Biphenyl)-3-ol	506	786	971	801
4,4'-Methylenebis-phenol	614	657	943	688
1,2-Benzene dicarboxylic acid dioctyl ester	684	645	820	759

Table 3. *GC-MS Computer Match Summary Hydrophobic Basic Fraction of Water Sample No. 1*

Compound	Peak No.	Purity	Fit	Reverse Fit
Phenol	69	855	932	904
2-Methylphenol	86	952	984	952
3-Methylphenol	91	929	918	936
4-Methylphenol	99	862	940	893
Aniline hydrochloride	76	743	848	828

Table 4. *GC-MS Computer Match Summary Hydrophobic Acidic Fraction of Water Sample No. 1*

Compound	Peak No.	Purity	Fit	Reverse Fit
Cyclohexenone	52	530	782	637
Anisole	59	884	985	892
Phenol	74	900	900	900
2-Methylphenol	98	943	989	943
Aniline	84	836	980	881
Dimethylphenol isomer	135	764	927	787

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Table 5. *GC-MS Computer Match Summary Hydrophilic Neutral Fraction of Water Sample No. 1*

Compound	Peak No.	Purity	Fit	Reverse Fit
Xylene	49	653	962	875
1-Chloro-2,4-dimethyl benzene	93	884	997	884
2-Methyl-2-cyclopenten-1-one	124	545	879	606
4,7 Dimethyl undecane	207	860	952	869

Table 6. *GC-MS Computer Match Summary Hydrophilic Basic Fraction of Water Sample No. 1*

Compound	Peak No.	Purity	Fit	Reverse Fit
Anisole	59	885	989	894
Phenol	77	901	959	935
Chloroxylene isomer	91	831	972	854
2-Methylphenol or isomer	99	942	996	942
3-Methylphenol or isomer	105	927	994	928
1-Bromo-2-methoxy-benzene	146	774	961	792

sample. The complete data are on file in this laboratory, and are open to perusal at any request. The mass spectrum of each peak is matched with the spectra of the three best match candidates. Alongside the spectra is the library search information summary for that peak.

Results

In the analysis of wastewaters from coal conversion processes taken as scrubber water from a coal hydrocarbonization process and a recycle process water, this fractionation method has provided for separated fractions totaling 80.3 and 92.5% of the original for the two different samples as shown in Table 1. In addition to these attractive values, this procedure has yielded separated fractions that may be analyzed suitably by GC/MS (Finnigan Company). This is indicated by the many compounds identified in the preliminary summary. In the hydrophobic fractions of sample No. 1, 19, 5, and 6, compounds were found in the neutral, basic, and acidic fractions (Tables 2 through 4), respectively. In the hydrophilic fractions, 4, 6, and 11, compounds were identified in the neutral, basic, and acidic fractions (Tables 5 through 7), respectively. These numbers represent the computer library-matched compounds. Other compounds were identified with less confidence in their quantitative assessment, and these are shown in the documented report.

In this study many of the PAH compounds except benzo(a)pyrene in wastewater samples were identified and quantified. The concentration of PAH compounds is in the microgram per liter range. Estimate quantities of the PAH's are shown in Table 8.

The major organic portion of coal consists of phenolic compounds. Thus, combined with this and the fact that for a typical pilot plant, the daily output of phenolics is about 10,000 Kg; it is not surprising that phenols comprise up to 90% of the total organic content of process wastewater. Phenolic type compounds are found mostly in the acid fractions of both the hydrophobic and hydrophilic group.

Phenol, cresol, xylenol are the major phenolic type compounds which also appear on the USEPA list of priority pollutants. Other phenolic compounds, including ethylmethyl phenol, ethyl phenol, and other polyalkyl phenols have also been found in the qualitative analysis. There are many isomers of these species in the coal wastewater samples; also the hydroxyl-substituted biphenyls have been detected.

The nitrogen content of most coals is generally below 2% and the nitrogen compounds are completely found as cyclic structures. These are the heterocyclic aromatic compounds and aromatic amines. In the qualitative analysis, aromatic amines are identified in all base fractions. The heterocyclic species, pyridine and quinoline type compounds, are found in the hydrophobic base fraction (Table 9). The concentration levels of nitrogen compounds are generally in the ppb range.

Chlorinated benzenes were identified in hydrophilic fractions of samples by qualitative analysis (Tables 10 and 11) for one sample. However, they have not been found in the quantitative analyses of GC/MS. Their existence can probably be explained by the presence of inorganic chlorine in the organic coal matrix, and subsequent interaction with the aromatic ring systems during the industrial processing.

Summary

Among the 129 priority pollutants listed by USEPA, 20 compounds were quantitatively identified in samples of coal liquefaction and gasification process wastewaters. Phenolic compounds are the dominant species, with levels as high as 2700 ppm for phenol, and 200 ppm for cresol as the next most prevalent species. Most species are in the $\mu g/L$, or ppb range. One notable exception is a hazardous nitrogenous compound, N-nitroso-dimethylamine, which exists at 1 ppm. In addition, a number of chlorinated benzenes have been found in the analyses of the hydrophilic fractions. The inorganic analysis of chemical properties in the two coal conversion wastewater samples has been made.

Recommendations

The current procedures are limited with respect to the range of molecular weights of the organic compounds in waste effluents. It is recommended that an interface of a high performance liquid chromatograph with a mass spectrometer, known as LC-MS, be used. This will increase the range of molecular weights to 1000 or beyond. Accurate assessment of environmental impact requires that these larger compounds not be neglected in this study. Organometallics of low volatility will also be detectable.

There are a number of advantages to LC separation. Separations may be

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Table 7. *GC-MS Computer Match Summary Hydrophilic Acidic Fraction of Water Sample No. 1*

Compound	Peak No.	Purity	Fit	Reverse Fit
Methyl hexanoic acid	54	843	939	891
Xylene	47	551	921	588
Anisole	60	901	999	901
Phenol	77	867	957	892
Chloroxylene isomer	91	865	989	865
3-Methylphenol	105	556	977	564
Methyl benzoate	116	827	962	858
1-Bromo-2-methoxy-benzene	145	793	962	806
Dimethyl pimelic acid	163	629	901	685
Methyl ester of benzenepropanoic acid	169	753	928	805
Dimethyl phthalate	234	644	915	687

Table 8. *Estimated Quantities of PAHs in Coal Liquid Water Extracts*

Compound	Concentration (µg/l)	Total Quantity Per day (gm)
Naphthalene	2.750	97.5
Anthracene	0.549	19.5
Phenanthrene	0.496	17.6
Pyrene	0.667	23.4
Benzo(a)anthracene	0.009	0.3
Chrysene	0.009	0.3
Fluoranthene	0.014	0.5

Table 9. *Compounds Identified from HO Base Fraction in Water Sample No. 2*

GC Scan No.	Base M/E	M.W.	Compound
37	93	93	Methylpyridine
48	107	107	2,6-Dimethylpyridine
54	93	123	Ethylpyridine
58	108	108	Phenylhydrazine
65	107	107	2,4-Dimethylpyridine
84	93	93	Aniline
86	93	93	4-Methylpyridine
112	106	143	2-Methylaniline hydrochloride
129	132	147	2-Methyl-2,3-dihydro-IH-indole
141	106	121	5-Methyl-3-ethylpyridine
160	118	133	5,6,7,8-Tetrahydroquinoline
171	129	129	Quinoline
187	143	143	2-Methylquinoline
196	132	133	1,2,3,4-Tetrahydroquinoline

based on polarity and/or molecular size. In polarity separations, columns including Corasil, Micro-Porasil, normal phase Micro-Bondapack-NH_2, reverse phase Micro-Bondapak-C_{18}, and aqueous compatible size exclusion columns can be used. In molecular size separation, Micro-Styrogel columns can be considered for use.

Another improvement in the analysis of these multicomponent systems is the use of extremely long (greater than 100 meters) lengths of capillary glass columns. Resolution of mixtures into individual compounds is greatly improved, making accurate identification of constituents by mass spectroscopy more likely. An extension of sensitivity of the lower end of the quantity range occurs, thereby reducing the relative error in quantitation and improving precision. Determination of extremely small concentrations is justified since extremely large quantities of wastewater produced daily may accumulate small concentrations of toxic substances to a hazardous daily output.

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Table 10. Compounds Identified from HI Neutral Fraction in Water Smaple No. 1

GC Scan No.	Base M/E	M.W.	Compound
49	91	106	1,2-Dimethylbenzene
93	105	140	1-Chloro-2,4-dimethylbenzene
124	96	96	3-Methyl-2-cyclopenten-1-one
207	57	184	4,7-Dimethylundecane

Table 11. Compounds Identified from HI Base Fraction in Water Sample No. 1

GS Scan No.	Base M/E	M.W.	Compound
77	94	94	Phenol
91	105	140	1-Chloro-2,4-dimethylbenzene
146	186	186	1-Bromo-2-methoxybenzene
205	57	184	5-Methyl-5-propylnonane

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The complete report, entitled "Analytical Methods for Hazardous Organics in Liquid Wastes from Coal Gasification and Liquefaction Processes," (Order No. PB 82-208 273; Cost: $10.50, subject to change) will be available only from:
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